Annex US.II, page 1

U.S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE TRANSMITTAL LETTER TO THE UNITED STATES 342.1.005 DESIGNATED/ELECTED OFFICE (DO/EO/US) U.S. APPLICATION NO. (If known, see 37 CFR 1.5) CONCERNING A FILING UNDER 35 U.S.C. 371 RNATIONAL APPLICATION NO. INTERNATIONAL FILING DATE PRIORITY DATE CLAIMED 24 September 1998 PCT/EP98/06056 26 September 1997 TITLE OF INVENTION MAGNETICALLY SHIELDED CONTAINER APPLICANT(S) FOR DO/EO/US Aidam, Elke; Ebert, Michael; Grossmann, Otten, Ernst-Wilhelm; Rohe, Daniela; and Surkau, Reinhard. Tino; Heil, Werner; Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information: This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 4. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2)) is transmitted herewith (required only if not transmitted by the International Bureau). has been transmitted by the International Bureau. Ь. is not required, as the application was filed in the United States Receiving Office (RO/US). A translation of the International Application into English (35 U.S.C. 371(c)(2)). Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) are transmitted herewith (required only if not transmitted by the International Bureau). have been transmitted by the International Bureau. have not been made; however, the time limit for making such amendments has NOT expired. have not been made and will not be made. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). Items 11. to 16. below concern document(s) or information included: An Information Disclosure Statement under 37 CFR 1.97 and 1.98. An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. A FIRST preliminary amendment. A SECOND or SUBSEQUENT preliminary amendment. A substitute specification. A change of power of attorney and/or address letter. Other items or information: copy of International Search Report.

Annex US.II, page 2

PCT Applicant's Guide - Volume II - National Chapter - US

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| 17. The following   | lowing fees are s  |                                  | <del></del>                                    |              |                       | CA                                      | LCULATIONS              |          |
|   | 17. The following fees are submitted:  BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5) ):   |                                  |  |              |                       |   |                         |          |
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| Total claims  | 47   | - 20 =                           | 27   |              | X \$18.00             | \$                                      | 486.00                  |          |
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| Processing fee of<br>months from the o  | \$130.00 for furni<br>earliest claimed pr  | shing the Er                     | nglish translation later<br>37 CFR 1.492(f)).  | than _       | 20 30                 | \$                                      |                         |          |
|   |  |                                  | TOTAL NA                                       | TIONAL       |                       | \$                                      | 1326.00                 |          |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property                                    |  |                                  |  |              |                       | , |                         |          |
|   |  |                                  | TOTAL FEES                                     | ENCLO        | OSED =                | \$                                      |                         |          |
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|   |  |                                  |  |              |                       |   | charged                 | \$       |
| a. A check in the amount of \$\_1326.00 \ to cover the above fees is enclosed.  |  |                                  |  |              |                       |   |                         |          |
| b. Please charge my Deposit Account No in the amount of \$ to cover the above fees. A duplicate copy of this sheet is enclosed.   |  |                                  |  |              |                       |   |                         |          |
| c. The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-0510. A duplicate copy of this sheet is enclosed.       |  |                                  |  |              |                       |   |                         |          |
| NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status. |  |                                  |  |              |                       |   |                         |          |
| SEND ALL CORRESPONDENCE TO  |  |                                  |  |              |                       |   |                         |          |
| WATOV & KIPNES, P.C. SIGNATURE  |  |                                  |  |              |                       |   |                         |          |
| P.O. Box 247  |  |                                  |  |              |                       |   |                         |          |
| Princeton Junction, New Jersey 08550 Alle   |  |                                  |  |              | ALLE                  | ı R.                                    | Kipnes                  |          |
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# 430 Rec'd PCT/PTO 2 3 MAR 2000

## ARK:jsg032200/3421005.PAMD

# IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

ة: <sub>بال</sub>مانية

**Applicant** 

Aidam, Elke; Ebert, Michael; Grossman, Tino;

Heil. Werner; Otten, Ernst-Wilhelm; Rohe, Daniela; and Surkau Reinhard

Serial No.

Filed Herewith

Filed

Filed Herewith

For

MAGNETICALLY SHIELDED CONTAINER

Attorney Docket No.

342.1.005

EXPRESS MAIL CERTIFICATE DATE March 23, 2000

LABEL NO. EL336356715US

I HEREBY CERTIFY THAT, ON THE DATE INDICATED ABOVE, I DEPOSITED THIS PAPER OR FEE WITH THE U.S. POSTAL SERVICE AND THAT IT WAS ADDRESSED FOR DELIVERY TO THE COMMISSIONER OF PATENTS & TRADEMARKS,

WASHINGTON, DC 20231 BY "EXPRESS MAIL POST OFFICE TO ADDRESSEE" SERVICE. Jill S. Garretson

NAME (PRINT)

Honorable Commissioner of Patents

March 23, 2000

and Trademarks Washington, D.C. 20231

#### PRELIMINARY AMENDMENT

Dear Sir:

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Applicants respectfully request that the above-identified application be amended as follows.

#### IN THE CLAIMS:

Please amend the following claims.

### ARK:jsg032200/3421005.PAMD

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Claims 3-5, line 1 cancel "either of claims 1 and 2" insert --claim 1--;

Claims 6-8, line 1 cancel "any one of claims 1 to 5" insert --claim 1--;

Claim 9, line 1 cancel "any one of claims 1 to 8" insert --claim 1--;

Claims 10 and 11, line 1 cancel "any one of claims 1 to 9" insert --claim 1--;

Claims 12, 14 and 16, line 1 cancel "any one of claims 1 to 11" insert --claim 1--;

Claim 18, line 1 cancel "any one of claims 1 to 17" insert --claim 1--;

Claim 19, line 1 cancel "any one of claims 1 to 18" insert --claim 1--;

Claims 20-25, lines 1-2 cancel "any one of the preceding claims" insert --claim 1--;

Claim 27, lines 1-2 cancel "any one of the preceding claims" insert --claim 1--; Claim 31, lines 1-2 cancel "any one of claims 27 to 30" insert --claim 27--; Claim 32, lines 1-2 cancel "any one of claims 27 to 31" insert --claim 27--; Claim 33, line 1 cancel "any one of claims 27 to 32" insert --claim 27--; Claim 34, lines 1-2 cancel "any one of claims 27 to 33" insert --claim 27--; Claims 36 and 37, lines 1-2 cancel "any one of claims 27 to 35" insert --claim 27--

Claims 38 and 39, lines 1-2 cancel "any one of the preceding claims" insert -- claim 1--;

Claims 42-44, lines 1-2 cancel "any one of the preceding claims" insert --claim 1--; and

Claim 47, line 3 cancel "any one of claims 1 to 38" insert --claim 1--.

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#### **REMARKS**

The foregoing amendment is submitted to remove multiple dependent claims from the original text of the application. Entry of the amendment is deemed proper and is respectfully requested. Calculation of fees due in the present application should be made based on the amended claims.

Any additional fees or credit for overpayment should be charged to Deposit Account No. 23-0510.

Respectfully submitted,

Address All Correspondence to: Allen R. Kipnes, Esquire WATOV & KIPNES, P.C. P.O. Box 247 Princeton Junction, NJ 08550 (609)243-0330 Allen R. Kipnes/Esquire Registration No. 28,433 Attorney for Applicant 6/prs

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WO 99/17304

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# MAGNETICALLY SHIELDED CONTAINER

The invention relates to a magnetically shielded container, e.g. usable as a transport device for spin polarized gases, and to a storage cell useful therein.

Nuclear spin polarized gases, in particular noble gases such as the helium isotope with the mass number 3  $(^{3}\text{He})$ or the xenon isotope with the mass number 129 ( $^{129}\mathrm{Xe}$ ) and gases containing the fluorine, carbon or phosphorus isotopes <sup>19</sup>F, <sup>13</sup>C or <sup>31</sup>P are required for a great number of experiments in fundamental physics research. In the field of medicine, such isotopes are, in particular, considered for use in nuclear magnetic resonance imaging, of the lungs for example. (See for example WO 97/37239, WO 95/27438, Bachert et al., Mag Res Med <u>36</u>: 192-196 (1996) and Ebert et al., The Lancet <u>347</u>: 1297-1299 (1996)). A prerequisite for the use of such spin polarized gases in nuclear magnetic resonance imaging is that the degree of polarization P of the spin I of the nuclei, or the associated magnetic dipole moment  $\mu_{\text{I}}$ , is greater by an order of 4-5 than is normally achieved in thermal equilibrium in the magnetic field  $\boldsymbol{B}_{\!\scriptscriptstyle T}$  of the magnetic resonance imaging apparatus. This normal degree of polarization,  $P_{\text{Boltzmann}}$ , is dependent on the magnetic dipole energy  $-\mu_{\scriptscriptstyle \rm I} B_{\scriptscriptstyle \rm T}$  and average thermal energy kT:

 $P_{Boltzmann} = tanh (\mu_I B_T / kT)$  (1)

(where k = Boltzmann's constant, and T = absolute temperature).

Where  $P_{Boltzmann}$  << 1, then it approximates to  $\mu_{\text{I}}B_{\text{T}}/kT$ .

Whereas the hydrogen isotope  $^1H$  used in magnetic resonance imaging of tissues only reaches a  $P_{\text{Boltzmann}}$  of 5

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x 10<sup>-6</sup> at  $B_T$  = 1.5 T and T = 300 K, a P $\ge$  1x10<sup>-2</sup>, i.e. 1%, is required in gas magnetic resonance imaging. The requirement for such an extremely increased P primarily results from the low concentration of the gas atoms in comparison with that of the hydrogen in the tissue. Gases with such degrees of polarization (normally referred to as hyperpolarized gases) can be produced by means of various known methods, preferably optical pumping.

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In addition, for gas magnetic resonance imaging relatively large quantities of gas, of the volume of a breath for example (0.5 to 1 litre), are needed.

- Particularly high degrees of polarization, for example >30%, combined with high rates of production, e.g. 0.5 litres/h, may be achieved through compression of an optically-pumped gas. This process is described in the following publications, the content of which is incorporated herein by reference:
  - Eckert et al., Nuclear Instruments and Methods in Physics Research <u>A 320</u>: 53-65 (1992);
- 25 Becker et al., J. Neutron Research <u>5</u>; 1-10 (1996);
  - Surkau et al., Nuclear Instruments and Methods in Physics Research A 384: 444-450 (1997);
  - 30 Neil et al., Physics Letters <u>A 201</u>: 337-343 (1995).

However production and use of hyperpolarized gases do not necessarily occur at the same site and the problem thus arises of transporting the polarized gases, produced for example using the method described above, to the consumer, for example for use in a nuclear magnetic resonance imaging apparatus for the lungs.

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Previously, transportable magnetic devices which provide a sufficiently homogeneous magnetic holding field for a large storage volume of such a spin polarized gas were not available. Furthermore, the nuclear spins very rapidly depolarized on the cell walls, so that polarized gases could only be stored for a short time while retaining the necessary degree of polarization.

One problem addressed by the invention is to provide a magnetic device capable of providing a transportable, homogeneous magnetic holding field for a sufficiently large storage volume of hyperpolarized gas.

Viewed from one aspect the invention thus provides a magnetically shielded container having disposed in parallel opposed position on an axis thereof magnetic field homogenizing pole shoes, having disposed about said pole shoes a magnetically shielding yoke, said pole shoes and yoke enclosing a magnetic chamber, said container further comprising magnetic field sources disposed about and radially distanced from said axis whereby there exists within said chamber a substantially homogeneous magnetic field  $B_o$  oriented in the direction of said axis and whereby there is a usable volume within said chamber where the ratio of the magnetic field gradient in the direction transverse to said axis to said magnetic field  $B_o$  has a value of no more than 1.5 x  $10^{-3}/cm$ .

30 Such a container may be constructed in a form which is low in weight, simple in structure, and inexpensive to manufacture and economical in use. Furthermore, using the container, nuclei which are transported can, as far as possible, retain their orientation, even in external stray fields, i.e. the depolarization relaxation times may be as long as possible in order to prevent a disorientation of the nuclear spin of the gas.

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The container of the invention, which is suitable for containing and transporting spin polarized atoms, especially polarized  $^3\text{He}$  and  $^{129}\text{Xe}$ , is preferably provided with magnetic field homogenising, highly-permeable and magnetically soft plates, e.g. of  $\mu\text{-metal}$  or soft iron, as pole shoes, and is so structured that a very large ratio can be achieved between the usable volume, within which a sufficiently homogeneous magnetic field is present, and the total volume, e.g. a ratio of at least 1:30. However, this ratio is preferably at least 1:5, more preferably 1:3 and, particularly advantageously 1:2. A ratio of 1:1.5 can be achieved. A value of

$$G_r = ((\delta B_r/\delta r)/B_o) \le 1.5 \times 10^{-3}/cm$$
 (2)

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is hereby applied as a homogeneity condition within the usable volume for the relative transverse gradient  $G_r$  of the magnetic field  $B_o$ . This requirement results from the gradient-dependent relaxation time  $T_{1G}$ , which (at high pressures, such as those the present invention is concerned with) is related as follows to  $G_r$  and the gas pressure p:

$$T_{1G} = p/G_r^2 \times (1.75 \times 10^4 \text{ cm}^2\text{bar/h})^{-1}$$
 (3)

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(see Scherer et al., Phys Rev <u>139</u>: 1398 (1965)).

According to equation (3), with  $G_r < 1.3 \times 10^{-3}/cm$  and p = 3 bars, a gradient-dependent relaxation time  $T_{1G} > 76~\rm h$  is achieved.

At lower pressures,  $T_{1G} = p/G_r^2 \times (1.8 \times 10^3 \text{ cm}^2\text{bar/h})^{-1}$  (see Barbe, Journal de Physique 35: 699 and 937 (1974)).

During the movement of a polarized gas storage cell into the container of the invention,  $G_r$  will generally be less than 0.02 x  $10^{-3}/cm$ . In this way  $^3He$  at 3 bar loses only

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2% polarization per 30 seconds.

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Within the container according to the invention,  $G_r$  is preferably no more than 1.3 x  $10^{-3}/\text{cm}$ , more preferably no more than 7 x  $10^{-4}/\text{cm}$ . With a gas storage cell radius of 8 cm,  $G_r$  of  $\leq$  1.3 x  $10^{-3}/\text{cm}$  corresponds to  $T_{1G}$  of  $\geq$ 127 hours, while with a gas storage cell radius of 2 cm,  $G_r$  of  $\leq$  7 x  $10^{-4}/\text{cm}$  corresponds to  $T_{1G}$  of  $\geq$  350 hours.

In order to compensate field distortions in the marginal areas of the interior space of the container and thus improve the homogeneity of the magnetic field Bo, the container features magnetic field sources which are arranged in such a way that the field distortions in the marginal areas of the interior space of the container are minimal and the field in the interior of the container is largely homogeneous.

In order to maintain the polarization of the nuclear spin once it has been achieved, only a relatively weak homogeneous magnetic field is required which preferably displays a magnetic field strength of less than 5 mT, more preferably less than 1 mT, more especially in the range 0.2 to 0.9 mT. In such a weak magnetic field, continuous quality control of the degree of polarization can be achieved with the aid of measuring instruments, ensuring particular reliability. Thus in one preferred embodiment, a magnetic field sensor (e.g. one based on the Förster principle) is disposed in the container of the invention so as to allow determination of the magnetic field  $B_{\rm d}$  generated by the hyperpolarized gas.

Whereas the generation of strictly homogeneous magnetic fields with the aid of ferromagnetic materials previously concentrated on high field strengths within the tesla range, the concept behind the container of the invention is deliberately focused on the most efficient

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and practical realisation of a weak, widely homogeneous magnetic field, e.g. using ferromagnetic materials.

A high degree of homogeneity can be achieved within the weak field range if, for example, as homogenising ferromagnetic elements, two thin soft iron, or more preferably  $\mu$ -metal, plates are used as pole shoes. Such pole shoes, thanks to their extremely high permeability and low remanence, create a very homogeneous field within the intervening space, the magnetic chamber.

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In a particularly preferred embodiment, the homogenising effect of these pole shoes can be increased by introducing magnetic resistances between the pole shoes and the yoke. A preferred material for a magnetic resistance of this sort, is a rigid non-magnetic layer, for instance in the form of a plate, for example of plastic, fitted between the pole shoe and yoke. If such a plate or, in order to save weight, preferably a porous, e.g. honeycomb structure, is also bonded to the pole shoe, this guarantees its flatness which allows the pole shoes to be parallel and the field B<sub>o</sub> to be homogeneous.

25 In order to fulfil the aforementioned homogeneity conditions in the simplest possible manner, and at the same time to provide a large storage volume, it has proved especially preferable to design the container of the invention in the form of a pot magnet. A magnetic device of this sort consists essentially of a closed pot 30 which, in an exemplary construction form, can have a diameter of 30-60 cm with an overall height of 10-30 cm. The particular advantage of designing the container in the form of a pot magnet lies in the high degree of 35 symmetry of this cylindrical construction. possibilities can be considered as particularly preferred arrangements of the field sources in a pot

magnet of this sort:

- positioning the field sources, for example in the form of commercially-available permanent magnetic plates, in a gap in the median or reflection plane of the pot; and

- positioning the field sources on the outer surface of the end plates of the pot.

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By appropriately dividing the field sources between these two arrangements, on the one hand positioning the field sources in the median plane, on the other hand positioning the field sources on the outer surface of the end plates of the pot, it is possible to correct the boundary errors of the magnetic field inside the pot magnet and thus fulfil the homogeneity conditions over a wide range in a radial direction. A preferred division is such that the increase in the boundary field which occurs when the field sources are arranged in the reflective or median plane of the pot magnet is just compensated by the fall-off in the boundary field which occurs where the field sources are positioned on the end plate of the pot.

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If desired, magnetic field sources may be placed elsewhere in the container of the invention so as to achieve an improvement in the homogenization of the applied field B<sub>o</sub>. Thus for example such sources may be placed in further planes perpendicular to B<sub>o</sub> besides the planes of, adjacent to and mid-way between the pole shoes.

A particularly homogeneous boundary field is also achieved if a magnetic screen, e.g. a soft iron or  $\mu$ -metal ring, is fitted between the pot and the rim of the pole shoe, so that an external stray field is partially

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short-circuited and, where the field sources are arranged on the median plane of the pot magnet, the value of the boundary field is reduced to the value of the central field in the centre of the pot magnet through appropriate dimensioning of the magnetic screen.

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Advantageously, especially in the case of non-circular cylindrical (e.g hexagonal-cylindrical) containers according to the invention, shims (e.g. corner shims-positioned onto the pole shoes) may be used to improve field homogeneity within the magnetic chamber.

Advantageously also the chamber has a high degree of azimuthal symmetry.

Two preferred construction forms can be used as magnetic 15 field sources. In a first construction form, permanent magnets can be used, preferably commercially-available tablets, for example with a height of 5 mm and a diameter of 20 mm. In another construction form, these permanent magnets are replaced with appropriately-20 dimensioned magnetic field coils. Such magnetic field coils have the advantage that the desired magnetic fields can be adjusted by means of an appropriatelyselected current flow. However, a disadvantage of the second construction form is that an additional current 25 source must be carried with the container where it is used as a transport device rather than simply as a storage device.

30 The container is advantageously constructed using a yoke of a material which is not magnetically saturated at fields below 1 Tesla, more preferably 2 Tesla, e.g. a soft iron. The container dimensions are preferably such that the usable volume (within which the gas storage cell may be disposed) is at least 50 mL, more preferably 100 mL, especially preferably 200 mL to greater than 1 m<sup>3</sup>, e.g. up to 20L, more particularly 200-2000 mL. The

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materials used can allow a total container weight to magnetic chamber volume of no more than 1 kg/L, more preferably 0.2 kg/L, especially preferably 1/30 kg/L. The gas storage cell which can be disposed in the container, e.g. for storage or transport, preferably has an internal volume of at least 50 mL, e.g. 100 mL to 1 m³, particularly 100 mL to 20L, more particularly 200 mL to 2L. This cell may be provided with a valve for allowing gas introduction and removal; alternatively it may be a single-use cell, e.g. provided with a sealable portion and a breakable portion (which may be the sealable portion after sealing).

In one embodiment, the container of the invention may take the form of a magnetic device with an internal space which provides a high-volume, largely homogeneous, shielded magnetic field within its interior, whereby the magnetic device features homogenising  $\mu$ -metal plates as pole shoes, the magnetic device is characterised in that a ratio of 1:1.5 can be achieved between the useable volume of the magnetic device within which a homogeneous magnetic field is present and the overall volume of the magnetic device and the homogeneity condition

 $G_r \leq 1.5 \times 10^{-3}/cm$ 

is fulfilled within the useable volume, where  $G_{\rm r}$  is the relative transverse magnetic field gradient.

Viewed from a further aspect, the invention also provides a gas storage cell containing a nuclear spin polarized gas in a gas storage space surrounded by a cell wall, the wall being of an uncoated material which on the surface contacting said gas storage space is substantially free of paramagnetic substances. The gas may for example be <sup>3</sup>He or <sup>129</sup>Xe, especially <sup>3</sup>He. Using an essentially paramagnetic substance free cell wall makes

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it possible for polarized <sup>3</sup>He to display a wall-related depolarization relaxation time  $T_1$  of at least 20 hours. It is particularly preferable that the wall-related depolarization relaxation time be more than 50 hours. Such high depolarization relaxation times can be achieved if a material is used as cell wall material which contains a low proportion of paramagnetic atoms or molecules, whereby in a particularly preferred construction form glasses with very low iron concentrations, preferably less than 20 ppm, are used, which can also be composed in such a way that, at the same time, they represent an efficient diffusion barrier against helium, for example Supremex glass (manufactured by Schott, Mainz, DE) of the type of the alumina silicate glasses. In comparison with the previouslyknown storage cells described by Heil et al. in Physics Letters <u>A 201</u>: 337-343 (1995), long wall-related depolarization relaxation times can be achieved using the storage cells in accordance with the invention, without complex metal coating of the walls being necessary.

As mentioned above, the container of the invention may take the form of a transport device for spin polarized gases, especially  $^3$ He and  $^{129}$ Xe or gases containing  $^{19}$ F,  $^{13}$ C or  $^{31}$ P, e.g. gases which have been spin polarized by polarization transfer. Within the area in the interior space of the container in which the storage cell is positioned, the magnetic field of the magnetic device can be so homogeneous that the depolarization relaxation time  $T_1^g$  caused by a transverse magnetic field gradient in accordance with equation (3) is greater than 125 hours, especially greater than 200 hours, more particularly greater than 300 hours, preferably greater than 500 hours, particularly preferably greater than 750 hours, and the wall-related depolarization relaxation time  $T_1^w$ , due to impacts of the nuclear-polarized gas on

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the wall of the storage cell, is greater than 5 hours, preferably greater than 20 hours.

More preferably,  $T_1^{\text{w}}$  normalized by the interior surface to volume ratio of the storage cell is preferably at least 10 h/cm.

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However, depolarization losses occur not only during the transport of the gas, due to the influence of external stray magnetic fields and the resulting inhomogeneity of the magnetic field, or due to collisions between the atoms and the wall, but, in particular, also when the gas is removed from the transport container.

- Viewed from a still further aspect, the invention therefore provides a method for the removal of a nuclear spin polarized gas from a gas storage cell in a container comprising:
- 20 (i) positioning said container with said axis parallel to the field direction of an external substantially homogeneous magnetic field;
- (ii) opening said container by removing a portioncomprising one of said pole shoes; and
  - (iii) removing said cell in the direction of said axis.

Such depolarization losses can be minimised if the removal of the polarized gas takes place according to this method.

In this method, the container, e.g. in the form of a pot magnet, is set up with its axis and the alignment of the internal, homogeneous magnetic field parallel to an external, adequately homogeneous magnetic field, which can, for example, be achieved with the aid of a Helmholz

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coil or the stray field of a nuclear magnetic resonance imaging apparatus. The half of the pot magnet facing the homogeneous magnetic field in an axial direction is then lifted off. The remaining half then guarantees a sufficient field homogeneity in the area of the gas cell through the magnetic equipotential surface of its pole shoe, which is made, for instance, of  $\mu$ -metal. The removal of the storage cell filled with polarized gas from the magnet can take place in an axial direction within a few seconds.

Embodiments of the invention are described by way of non-limiting Examples, with reference to the accompanying drawings, in which:

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- Fig. 1: shows an external perspective view of the container of the invention;
- Fig. 2: shows a cross section through a container in accordance with the invention, which is in pot magnet form and contains a storage cell for spin polarized gases positioned within its interior;
- Figs. 3a-d: show various arrangements for boundary field compensation;
  - Fig. 4: shows a further variant of the container in accordance with the invention;

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Fig. 5a: shows the curve of the value of the relative, radial gradient  $G_{\rm r}$  in the radial direction R of a pot magnet for different arrangements of the field sources;

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Fig. 5b: shows the curve of Figure 5a with the scale modified for emphasis;

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Fig. 6: shows the relaxation of <sup>3</sup>He polarization in a storage cell made of of glass with a low iron content, whereby the volume of the cell is, for example, 350 cm<sup>3</sup> and the gas pressure 2.5 bars;

- Figs. 7a-b: demonstrate the removal of a storage cell from a container according to the invention placed within an external field; and
- Fig. 8: shows a further variant of a container according to the invention which has non-circular cylindrical symmetry.

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- 15 Referring to Figure 1, there is shown an external perspective view of a container 1 in accordance with the invention, which in this instance is designed as a twopart cylindrical pot magnet with an upper section 1.1 and a lower section 1.2. Also indicated is the rotationally symmetrical axis S of the pot magnet and 20 the magnetic field line of external magnetic fields, for example the earth's magnetic field. Especially clearly shown is the path of an external magnetic field or stray field B, which does not penetrate into the interior of 25 the pot magnet but, due to the slight magnetic resistance of the yoke 2, which is preferably made of soft iron material, is conducted around the interior space. The stray field Bs is perpendicular to the endplates of the yoke and is homogenised by the  $\mu\text{-soft}$  iron 30 pole shoes positioned inside the yoke 2.
- Figure 2 shows an axial cross section through a container for spin polarized gases, especially <sup>3</sup>He, <sup>129</sup>Xe, as shown in Figure 1, comprising the container in accordance with the invention and a storage cell for spin polarized gas positioned inside it, which is characterised by extremely long wall depolarization

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relaxation times.

The pot magnet 1 comprises a cylindrically-formed yoke 2, preferably made of soft iron for returning the 5 magnetic flux and for shielding off external fields. turn, the cylindrically-formed yoke 2 features two yoke end plates forming a central section 2.1. construction form shown, the yoke end plates 2.1 take the form of two circular discs 2.1.1 and 2.1.2. Closed surrounding sheets 2.2 and 2.3 are arranged around the 10 rim of the yoke end plates to form a yoke jacket. differ in the two construction forms shown in the left and right halves of Fig. 2. The surrounding sheets 2.2 and 2.3 are arranged both on the upper disc 2.1.1 and also on the lower disc 2.1.2, resulting in an upper 15 section and lower section of the pot magnet, which, in the first construction form shown on the left, meet at the projecting angled peripheral flanges 2.2.1 in the median plane of the magnetic device. In the second construction form shown on the right, the peripheral 20 flanges 2.3.1 are spaced in such a way that an opening for holding field sources, for example permanent magnets, is formed in the median plane 4 of the pot magnet 1. The field line produced due to the 25 positioning of the field sources, for example the permanent magnets, in the centre between the upper and lower peripheral flanges of the pot magnet is identified with 6. In the first construction form shown on the left, the height of the two halves of the yoke jacket 30 2.2 exceeds the distance between the yoke end plates 2.1.1, 2.1.2. It is possible to position field sources on the outer surface 2.5 in the gap between the jacket and end plate. The field line in the boundary region which results with such an arrangement is identified 35 with the number 8.

The two opposing pole shoes 10.1 and 10.2 are

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responsible for the homogeneous field within the interior of the pot magnet. In this example, the pole shoes are essentially designed as homogenising  $\mu$ -metal plates.  $\mu$ -metal is a material with a very high homogenising force in relation to an external, stray magnetic field  $B_x^{\ II}$  and is distinguished by very low remanences.

In this example,  $\mu$ -metal A manufactured by Vacuumschmelze, P.O. Box 2253,63412 Hanau with the following magnetic characteristics is used:

|    | Stat. coercivity:      | $H_c$          | $\leq$ 30 mA/cm |
|----|------------------------|----------------|-----------------|
|    | Permeability:          | $\mu_{(4)}$    | ≥ 30,000        |
| 15 | Maximum permeability:  | $\mu_{(\max)}$ | $\geq$ 70,000   |
|    | Saturation inductance: | $B_2$          | $\geq$ 0.65 T   |

(This should not be interpreted as meaning that only this material can be used for the invention). Over the entire pole shoes, the distance between the shoes, and the parallel orientation of the pole shoes may be ensured by the provision of spacer elements or spacer rings, e.g. a total of three (or more) spacers 12, of which only one is shown in Figure 2.

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The resulting homogeneous magnetic field between the pole shoes 10.1 and 10.2, made of  $\mu$ -metal, is identified with the reference number 14 in this representation. As can be seen from the representation in Figure 1, a particularly homogeneous magnetic field, independent of external fields, is achieved inside the pot magnet due to the homogenising force of the  $\mu$ -metal, whereas, in the marginal areas, depending on the arrangement of the field sources, a different field pattern 6 or 8 occurs. If the field sources are arranged solely in the median plane 4, as shown for the right-hand marginal area of the pot magnet 1, then a considerable part of the

- 16 -

magnetic flux escapes from the jacket due to the low magnetic resistance and, acting from the edge, interferes with field between the pole shoes, with an amplifying effect. The field therefore increases significantly in intensity towards the edge, as a result of which the desired homogeneity is impaired even where the two pole shoes are a relative short distance apart. Where the permanent magnets are positioned on the outer surface on the end plates of the pot, as shown in Figure 2 for the left-hand half of the magnet, a significant marginal fall-off; of the field is observed between the pole shoes 10.1,10.2, as shown by the field line 8, because the jacket, which reaches right up to the pole shoes, attracts and weakens the boundary field.

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The very homogeneous field 14 produced in the intervening space due to the extremely high permeability of the  $\mu$ -metal plates used as pole shoes 10.1,10.2 can be increased even further through the introduction of a magnetic resistance 16 between the pole shoes 10.1, 10.2 and the yoke 2.1.1 and 2.1.2. A rigid, non-magnetic plate, for example a plastic plate 16 or, in order to save weight, preferably a honeycomb structure, is preferably used for this purpose. The plate 16 can be bonded to the pole shoes 10.1,10.2, thus guaranteeing the flatness of the pole shoes 10.1,10.2.

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The storage cell 20 for holding the polarized gas is located in the central mid-section of the pot magnet 1 between the two pole shoes 10.1,10.2. The container 20 is preferably manufactured of iron-free glass and has an iron concentration of less than 20 ppm, for example, and can also be designed in such a way that it also forms an efficient diffusion barrier against helium. This measure allows wall-related relaxation times of more than 70 hours to be achieved. The storage cells 20 can be pumped out prior to use and, for example, as is usual

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in high-vacuum technology, heated through until their residual water layers are lost. This measure is advantageous in the invention, but by no means necessary. The storage cells are, for example, sealed with a glass stopcock 22 and are connected to the filling unit for the polarized gas via a glass flange 24.

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cell.

In addition, in order to determine the degree of
polarization, a high-frequency coil 30 (which can be
used to subject the storage cell 20 to a time-variant
magnetic field) and a detection device (e.g. a magnetic
field sensor) 32 can be fitted as may means for moving
sensor and storage cell relative to each other.

However, these additional fixtures are optional and are
by no means essential for a transport device in

Furthermore, the container may if desired be fitted with cooling means to cool the contents of the gas storage

accordance with the invention.

The decisive feature of the invention is that a magnetic field is created within the container which is homogeneous over a very large volume, so that a high usable volume is achieved in relation to the total volume of the magnetic device, whereby the homogeneous field within the interior of the magnetic device is essentially not to be interfered with by external magnetic fields. On the one hand, the low magnetic field strength of  $B_{\rm o} < 1$  mT which may be used allows a very lightweight construction of the yoke and pole shoes using thin soft iron sheeting. On the other hand, it is desirable that the pole shoes display particularly low remanence, so that these are therefore preferably made of  $\mu$ -metal in order to fulfil the homogeneity requirement (2).

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In terms of being able to determine the degree of polarization, it is advantageous if the homogeneous holding field in the interior of the magnet is a weak magnetic field with a field strength of less than 1.0 mT, since the magnetic fields caused by the spin polarization of the gas, which lie within the nano to micro Tesla range, can then still be measured with sufficient accuracy with the aid of the simple detection device 32 and the degree of polarization determined on this basis. This is advantageous if, for example, the quality of the delivered gas has to be tested prior to a medical application.

Figure 3 shows the field distribution within the marginal area achieved by means of different arrangements of field sources, either alone or in combination with a magnetic screen, which guarantees a sufficiently homogeneous field distribution within the marginal area.

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Figure 3a shows an arrangement in which the permanent magnets are placed inside the gap 2.4 and inside the gap 2.5 on the end plates of the pot 2.1.1, 2.1.2. By dividing the arrangement of the permanent magnets 2.4. appropriately between arrangement in the centre 4 and arrangement on the end plates of the pot 2.1.1, 2.1.2, the increase in the intensity of the boundary field 6, which is caused by the positioning of the permanent magnets in the centre between the end plates of the pot, as shown, is just compensated by the fall-off in the intensity of the boundary field 8 of the permanent magnets arranged on the end plates of the pot. individual permanent magnets are of equal magnetic field strength, an optimal distribution of the permanent magnets is achieved, for the height-to-width ratio of the pot shown in the drawing, if the magnets are distributed in a numerical ratio of 6:8, whereby the

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first figure represents the number of magnets which are arranged in the median plane 4, and the second figure represents the number of magnets which are arranged on the end plates of the pot.

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Figure 3b shows a possible homogenisation of a boundary field using permanent magnets arranged in the median plane 4 with the aid of a magnetic screen 40. A magnetic screen of this sort is, for example, formed by a soft iron ring which is introduced between the pot and the rim of the pole shoe and which, like the sheets 2.2,2.3, runs around it. Such a soft iron ring partially short-circuits the stray external field and, if appropriately dimensioned, reduces the boundary field to the value of the central field.

Figures 3c and 3d show means of compensation which are comparable with Figures 3a and 3b where, in this example, magnetic coils 50,52 arranged centrally in the area of the median plane 4 of the pot or in the vicinity of the end plates of the pot are used as field sources instead of permanent magnets.

Figure 3c shows the compensation achieved through a suitable ratio of field sources arranged in the median plane to field sources arranged in the vicinity of the end plates of the pot, and Figure 3d shows the compensation with the aid of a magnetic screen 40.

A further construction form of the invention is shown in Figure 4. In order to reduce weight, the yoke jacket is constructed of very thin surrounding sheets 200.1,200.2 and 202.1 and 202.2, in a double-walled construction. The surrounding sheets 200.1, 200.2 and 202.1 and 202.2 are arranged at a fixed distance from one another using

spacing rings 207, so that a double shielding of the interior of the pot magnet 1 is achieved. These can be

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considerably thinner than in a single-walled construction form as shown in Figure 1, while displaying the same capacity to conduct magnetic fluxes away via the shielding rings. The surrounding sheets are connected with the upper or lower  $\mu$ -metal plate of the pot magnet via a screwed connection 204 or 206. pole shoes 10.1 and 10.2 are spaced apart by means of spacing elements or a spacing ring 205 which may be circular or polygonal, e.g. hexagonal, in cross-section. The homogeneous magnetic field is essentially formed in the interior 208 between the pole shoes. As in Figure 3a, the permanent magnets 210 fitted in the gap 2.4 between the upper and lower section of the pot magnet and between the jacket and end plate serve as sources for a field which is also homogeneous in the marginal area.

Figures 5a and 5b shows the curve of the amount of the relative, radial gradient  $G_r = ((\delta B_r/\delta_r)/B_o)$  measured 1.5 cm above the reflective plane 4 of the pot magnet in a radial direction r for different arrangements of the permanent magnets in or on the pot magnet in accordance with the invention. The curve marked "a" shows the curve produced when permanent magnets are only arranged in the gap in the median plane 4, as shown in the right half of Fig. 2, and the curve marked "b" shows the curve produced where the permanent magnets are positioned on the outer surface on the end plates of the pot as shown on the left-hand side of Fig. 2. The curve identified with "c" shows the curve of the radial gradient which is produced if the permanent magnets are divided between being positioned on the outer surface and being positioned in the gap in the median plane in accordance The numerical ratio between the magnets with Fig. 3a. is 6:8 in the curve shown in curve 3c, i.e. 6 magnets were arranged in the centre and 8 on the end plates. In this case, with a gap between the pole shoes of 18 cm

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and a pole shoe diameter of 40 cm, the homogeneity limit which is represented by the dotted band 400 achieves a value of  $G_r = 1.5 \times 10^{-3}$  with r approximately 13 cm, more preferably 12 cm. This limit 400 is displayed over the entire height of the pot magnet, so that a usable transport volume of more than 6 litres, e.g. more than 8 litres is provided within the pot magnet, in which the homogeneity condition  $G_r \leq 1.5 \times 10^{-3}/cm$  is fulfilled.

- Figure 6 shows a measurement record of the relaxation of 10 the <sup>3</sup>He polarization in a storage cell of glass with a low iron content. The volume of the storage cell is 350 cm<sup>3</sup>, the gas pressure 2.5 bars. As can be seen from this figure, a relaxation time of more than 70 hours is 15 measured through the use of such glasses, whereby the gradient-dependent relaxation time could be ignored under the conditions for this measurement. If one introduces such a receptacle consisting of glass with a low iron content into the pot magnet in the region of 20 the homogenised field, a resulting total relaxation time  $T_{res} = (1/T_1^9 + 1/T_1^w)^{-1}$  of 64 hours is achieved, based on a gradient-dependent relaxation time of  $T_1^{g} = 750 \text{ h}$  and a wall-related relaxation time of  $T_1^9 = 70 \text{ h.}$
- **25** The method of the invention for removing a gas stored in a storage cell 20 of a transport device in accordance with the invention in the vicinity of an external magnetic field, for example the stray field  $B_{TS}$  of a nuclear magnetic resonance imaging apparatus, is 30 represented in Figures 7a and b. If the storage cell is to be introduced into the field  $\boldsymbol{B}_{\!\scriptscriptstyle T}$  of the magnetic resonance imaging apparatus, for a medical application for instance, without this involving significant depolarization, the invention proposes, as illustrated 35 in Figure 7a, that the transport device in accordance with the invention be set up with its field  $\ensuremath{B_{o}}$  parallel to and in the same direction as the external magnetic

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The upper part of the transport field  $B_{TS}$ , as shown. device facing the magnetic resonance imaging apparatus with the pole shoe 10.1 is then lifted off in the direction indicated by the arrow 302. This makes the storage cell 20 freely accessible. The transport device, designed here in the form of a pot magnet, is shown in its opened state in Figure 7b. As can clearly be seen, the homogenising force is reduced due to the upper section of the pot magnet not being present. Nonetheless, the remaining lower pole shoe 10.2 ensures that the magnetic field lines of the resulting field Bres end perpendicular on this pole shoe. This still makes it possible to homogenise the magnetic field  $B_{\rm res}$ adequately in the area of the storage cell 20, i.e. to achieve parallel lines of magnetic force, as shown in the drawing. The storage cell can then be removed along arrow 304 in the direction of the symmetrical axis, in the field Bres which is still largely homogeneous even with the upper section removed, without a noticeable depolarization of the gas occurring during the brief time taken for removal.

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Referring to Figure 8 there is shown, in perspective, a container according to the invention with hexagonal-cylindrical, rather than circular cylindrical symmetry. Container 1 comprises a hexagonal-cylindrical yoke 2 and has separable upper 1.1 and lower 1.2 portions. Magnetic field sources, pole shoes, etc. may be disposed, e.g. as described for the variants described above, if necessary including shims to combat edge effects to field  $B_{\rm o}$ .

The gas contained in the storage cell designed in accordance with the invented method still possesses an adequate degree of polarization for the intended applications after being removed within the strong magnetic field of the nuclear magnetic resonance imaging

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apparatus.

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This invention thus provides a device which allows the storage and transport of spin polarized gases over long distances and periods, such as is required in particular for an intended use in the field of medicine. In particular, the invention is characterised by its economical construction, simple design, maximum possible useable volume and very low weight, whereby reliable shielding against external stray fields is provided. The invention thus provides, for the first time, a means which makes the commercial use of <sup>3</sup>He and <sup>129</sup>Xe feasible, in the field of medicine for example.

Regarding future possible uses of <sup>3</sup>He and <sup>129</sup>Xe in medicine, particular reference is made to the use of polarized <sup>3</sup>He and <sup>129</sup>Xe in brilliant, high-resolution, three-dimensional nuclear magnetic resonance imaging of the human respiratory system.

Regarding this application, reference is made to the following publications, the disclosed content of which is included in full in this application:

- Bachert et al., Magnetic Resonance in Medicine 36: 192-196 (1996); and
  - Ebert et al., THE LANCET <u>347</u>: 1297-1299 (1996).
  - In addition, a compact magnet of lightweight construction is presented which provides a magnetic field which is both homogeneous over a wide area, compact, easily transportable and relatively low in cost and which, in particular, also fulfils all requirements in terms of shielding off external magnetic fields which can lead to a depolarization of the nuclear spin. The use of commercially-available small permanent magnets

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represents a quite decisive advantage in terms of both construction and economy.

In addition, there is the extremely high permeability and low remanence of the  $\mu$ -metal which is in this case used for the first time for the construction of very thin, therefore lighter, and yet highly-efficient pole shoes for the homogenisation of the magnetic field.

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The low magnetic flux also allows the use of a yoke made of thin soft iron sheet which, at the same time, due to the pot form and the associated possibility of radial conduction, adequately shields off external interference fields.

This means that, in this invention, a magnet with an extremely favourable ratio of homogeneous field volume to total volume and very low weight is made available for the first time.

In a slightly inferior construction form, pole shoes of magnetically soft iron can be used in place of the  $\mu$ -metal pole shoes which, while reducing the quality of the field, represents a more economical variant in terms of price. It is also possible to replace the permanent magnets with magnetic field coils which fulfil the same function, in order to generate the necessary flux at the points required within the pot magnet.

Finally, a method for removing a spin polarized gas from the pot unit in accordance with the invention is described in which the degree of polarization is also maintained in the presence of external magnetic fields, for example those of a nuclear magnetic resonance imaging apparatus.

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#### Claims:

- 1. A magnetically shielded container (1) having disposed in parallel opposed position on an axis (S) 5 thereof magnetic field homogenizing pole shoes (10.1, 10.2), having disposed about said pole shoes a magnetically shielding yoke (2), said pole shoes and yoke enclosing a magnetic chamber (26), said container further comprising magnetic field sources (2.4,2.5) disposed about and radially distanced from said axis 10 whereby there exists within said chamber subsantially homogeneous magnetic field  ${\bf B}_{\rm o}$  oriented in the direction of said axis and whereby there is a usable volume within said chamber where the ratio of the magnetic field 15 gradient in the direction transverse to said axis to said magnetic field  $B_{\text{o}}$  has a value of no more than 1.5 x $10^{-3}/cm$ .
- 2. A container as claimed in claim 1 wherein said ratio has a value of no more than  $7 \times 10^{-4}/\text{cm}$ .
  - 3. A container as claimed in either of claims 1 and 2 wherein the ratio of the volume of said usable volume to the volume of said chamber (26) is greater than 1:30.
  - 4. A container as claimed in either of claims 1 and 2 wherein the ratio of the volume of said usable volume to the volume of said chamber (26) is greater than 1:5.
- 30 5. A container as claimed in either of claims 1 and 2 wherein the ratio of the volume of said usable volume to the volume of said chamber (26) is greater than 1:2.
- 6. A container as claimed in any one of claims 1 to 5 wherein the volume of said usable volume is at least 50 mL.

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- 7. A container as claimed in any one of claims 1 to 5 wherein the volume of said usable volume is at least 100 mL.
- 8. A container as claimed in any one of claims 1 to 5 wherein the volume of said usable volume is at least 200 to 2000 mL.
- 9. A container as claimed in any one of claims 1 to 8 wherein said pole shoes (10.1,10.2) are of  $\mu$ -metal or soft iron.
  - 10. A container as claimed in any one of claims 1 to 9 wherein said yoke (2) is of a material which is not magnetically saturatable at magnetic field strengths below 1 Tesla.
- 11. A container as claimed in any one of claims 1 to 9 wherein said yoke (2) is of a material which is not
   20 magnetically saturatable at magnetic field strengths below 2 Tesla.

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- 12. A container as claimed in any one of claims 1 to 11 wherein said magnetic field sources (2.5) are disposed around the peripheries of each of said pole shoes (10.1, 10.2).
  - 13. A container as claimed in claim 11 wherein said magnetic field sources are disposed between the side wall (2.2) and end walls (2.1.1,2.1.2) of said yoke.
    - 14. A container as claimed in any one of claims 1 to 11 wherein said magnetic field sources (2.4) are disposed about said axis (S) on a plane (4) between said pole shoes (10.1,10.2)

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- 15. A container as claimed in claim 14 wherein said magnetic field sources (2.4) are disposed between two sections (2.3) of said yoke (2).
- 5 16. A container as claimed in any one of claims 1 to 11 wherein one array of magnetic field sources (2.5) is disposed around the peripheries of each of said pole shoes (10.1,10.2) and a further array of magnetic field sources (2.5) is disposed about said axis (S) on a plane (4) between said pole shoes (10.1,10.2).
  - 17. A container as claimed in claim 16 wherein said arrays (2.4,2.5) of magnetic field sources are disposed as defined in claims 12 and 14.
- 18. A container as claimed in any one of claims 1 to 17 further comprising a magnetic screen (40) disposed about said axis (S) within said yoke (2).

- 19. A container as claimed in any one of claims 1 to 18 further comprising at least one shim disposed about said axis (S) within said yoke (2).
- 20. A container as claimed in any one of the preceding claims for which the ratio between the total weight of the container (1) and the volume of the magnetic chamber (26) is no more than 1 kg/L.
- 21. A container as claimed in any one of the preceding claims for which the ratio between the total weight of the container (1) and the volume of the magnetic chamber (26) is no more than 0.2 kg/L.
- 22. A container as claimed in any one of the preceding claims for which the ratio between the total weight of the container (1) and the volume of the magnetic chamber (26) is no more than 1/30 kg/L.

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- 23. A container as claimed in any one of the preceding claims which is openable and sealingly closable.
- 24. A container as claimed in any one of the preceding claims wherein said pole shoes (10.1,10.2) are circular and said yoke (2) is substantially cylindrical.
  - 25. A container as claimed in any one of the preceding claims wherein said pole shoes (10.1,10.2) are supported by magnetically resistant elements (16).
    - 26. A container as claimed in claim 25 wherein said elements (16) are of rigid porous plastic.

- 27. A container as claimed in any one of the preceding claims further comprising a gas storage cell (20) disposed in said usable volume in said magnetic chamber (26).
- 28. A container as claimed in claim 27 wherein at least the inner walls of said cell are formed of a material essentially free of paramagnetic substances.
- 29. A container as claimed in claim 28 wherein said material is a very low iron concentration glass.
  - 30. A container as claimed in claim 29 wherein said glass has an iron concentration of less than 20 ppm.
- 30 31. A container as claimed in any one of claims 27 to 30 wherein the walls of said cell (20) are uncoated.
- 32. A container as claimed in any one of claims 27 to 31 wherein the wall of said storage cell (20) is of a low iron content glass, the iron content being sufficiently low that the ratio between the wall-related depolarization relaxation time T<sub>1</sub>" for nuclear spin

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polarized  $^{3}$ He and the volume-to-inner surface area of said cell is at least 10 hours/cm.

- 33. A container as claimed in any one of claims 27 to 32 wherein said cell (20) is provided with a valve (22) to permit introduction and removal of gas.
  - 34. A container as claimed in any one of claims 27 to 33 wherein said cell (20) contains nuclear spin polarized gas.
    - 35. A container as claimed in claim 34 wherein said gas is  $^{3}\text{He}$  or  $^{129}\text{Xe}$  or contains  $^{19}\text{F}$ ,  $^{13}\text{C}$  or  $^{31}\text{P}$ .
- 36. A container as claimed in any one of claims 27 to 35 wherein said cell (20) has an internal volume of at least 50 mL.
- 37. A container as claimed in any one of claims 27 to 35 wherein said cell (20) has an internal volume of betweem 100 mL and 1 m<sup>3</sup>.
  - 38. A container as claimed in any one of the preceding claims in transportable form.
  - 39. A container as claimed in any one of the preceding claims further comprising a magnetic field sensor (32) disposed within said magnetic chamber (26).
- 40. A container as claimed in claim 39 further comprising means for moving said sensor (32) relative to a gas storage cell (20) disposed in said magnetic chamber (26).
- 41. A container as claimed in claim 39 further comprising a source (30) for a time variant magnetic field disposed in said magnetic chamber (26).

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42. A container as claimed in any one of the preceding claims further comprising a spacer (12,205) so disposed as to maintain said pole shoes (10.1,10.2) in parallel opposed relationship.

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43. A container as claimed in any one of the preceding claims having a double-hulled (200.1,200.2) construction whereby said yoke (2) is provided at least in part by the inner hull (200.2).

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condition

44. A container as claimed in any one of the preceding claims in the form of a magnetic device (1) with an internal space which provides a high-volume, largely homogeneous, shielded magnetic field within its interior, whereby the magnetic device (1) features homogenising  $\mu$ -metal plates as pole shoes (10.1, 10.2), wherein a ratio of 1:1.5 can be achieved between the useable volume of the magnetic device within which a homogeneous magnetic field is present and the overall volume of the magnetic device and the homogeneity

## $G_r \le 1.5 \times 10^{-3} / cm$

- is fulfilled within the useable volume, whereby  $G_r$  is the relative transverse magnetic field gradient.
  - 45. A gas storage cell (20) containing a nuclear spin polarized gas in a gas storage space surrounded by a cell wall, the wall being of an uncoated material which on the surface contacting said gas storage space is substantially free of paramagnetic substances.
- 46. A cell as claimed in claim 45 wherein said wall is of a low iron content glass, the iron content being sufficiently low that the ratio between the wall-related depolarization relaxation time T<sub>1</sub><sup>w</sup> for nuclear spin

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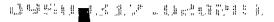
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polarized <sup>3</sup>He and the volume-to-inner surface area of said cell is at least 10 hours/cm.

- 47. A method for the removal of a nuclear spin polarized gas from a gas storage cell (20) in a container as claimed in any one of claims 1 to 38 comprising:
- (i) positioning said container with said axis (S) parallel to the field direction of an external substantially homogeneous magnetic field;
- (ii) opening said container by removing a portion comprising one of said pole shoes (10.1); and
- (iii) removing said cell (20) in the direction of said axis.

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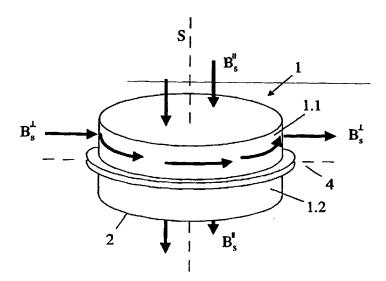
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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

#### **Published**

With international search report.

(54) Title: MAGNETICALLY SHIELDED CONTAINER

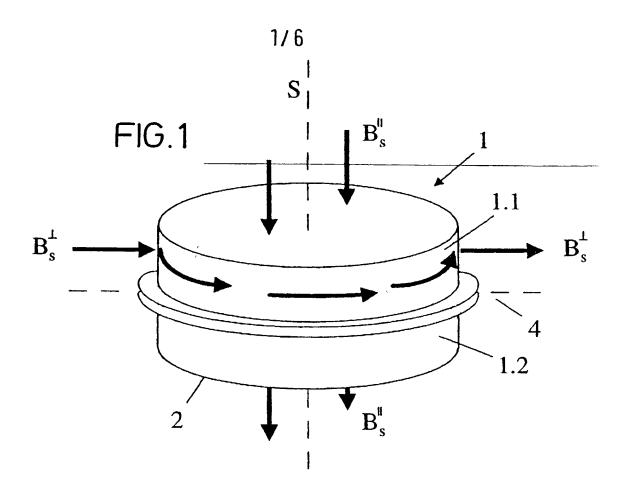


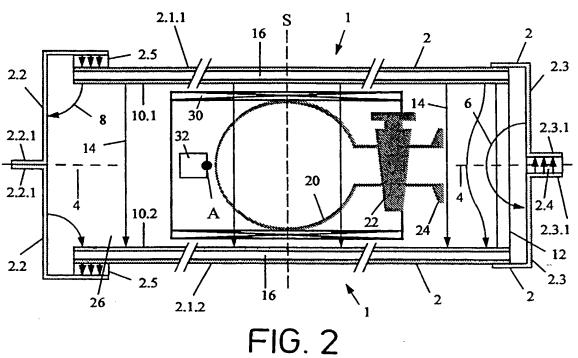
#### (57) Abstract

The invention provides a magnetically shielded container (1) having disposed in parallel opposed position on an axis (S) thereof magnetic field homogenizing pole shoes (10.1, 10.2), having disposed about said pole shoes a magnetically shielded yoke (2), said pole shoes and yoke enclosing a magnetic chamber (26), said container further comprising magnetic field sources (2.4, 2.5) disposed about and radially distanced from said axis whereby there exists within said chamber substantially homogenous magnetic field Bo oriented in the direction of said axis and whereby there is a usable volume within said chamber where the ratio of the magnetic field gradient in the direction transverse to said axis to said magnetic field Bo has a value of no more than 1.5 x 10-3/cm. By virtue of the very low ratio of weight to volume that is achievable with this construction, the containers according to the invention are economical to produce and especially suited to transporting polarized gasses.

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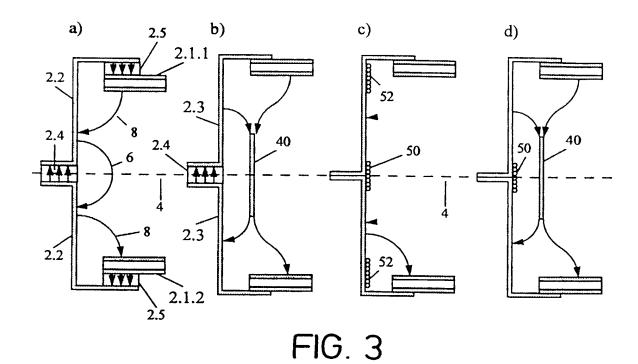


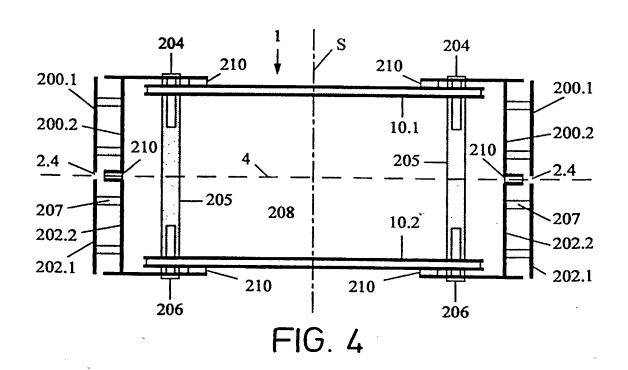
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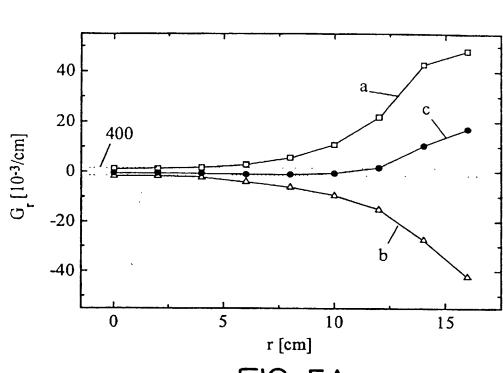
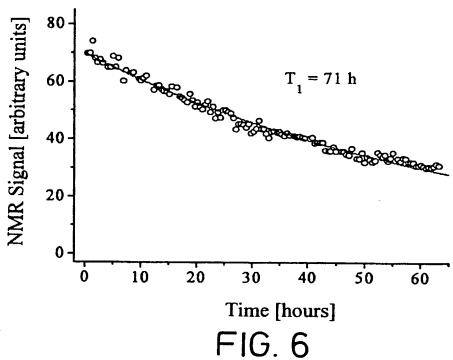


FIG. 5A

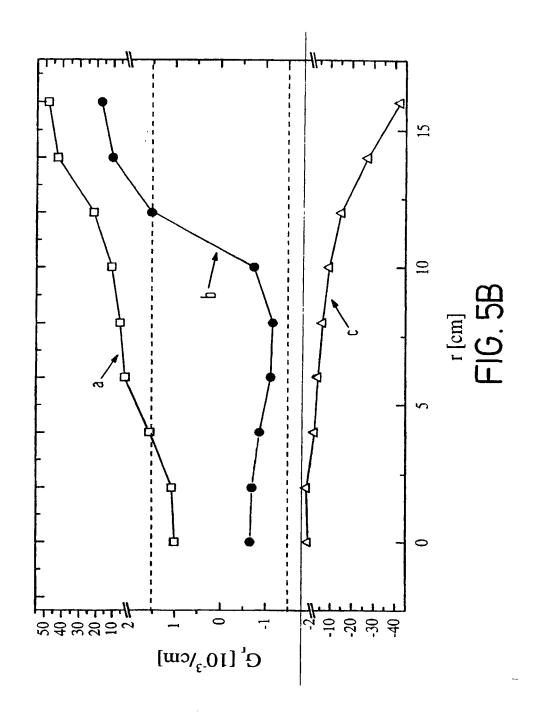


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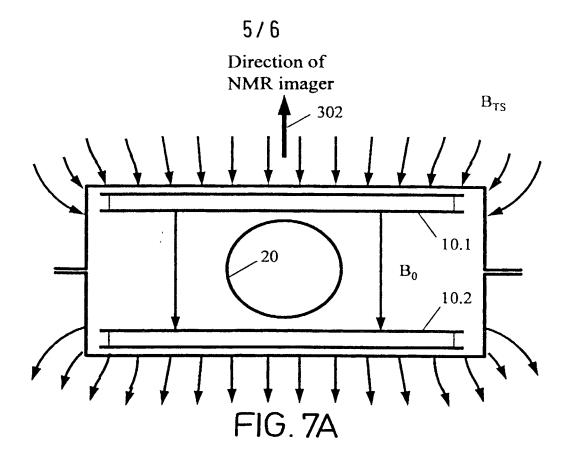
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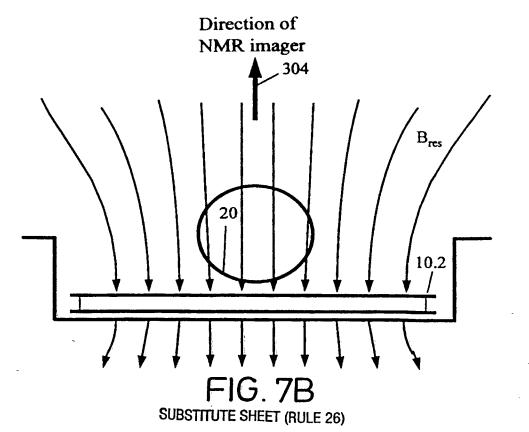
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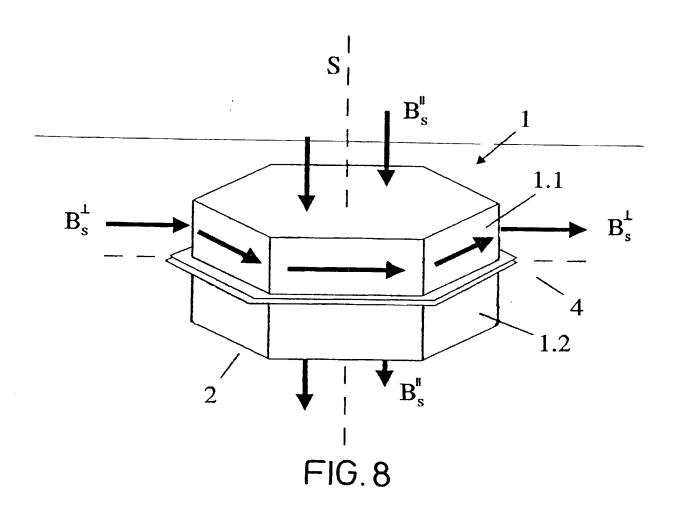




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UTILITY PATENT OR DESIGN

# DECLARATION AND POWER OF ATTORNEY (Sole or Joint)

ATTORNEY'S DOCKET NO. 342.1.005 (PL 9745)

| 101  | As a below named inventor, I declare that I believe I am the original, first and sole inventor if only one name is listed at Item 201 below, or a joint inventor if plural names are listed below at Items 201 et seq., of the subject matter which is claimed and for which a patent is sought on the invention entitled MAGNETICALLY SHIELDED CONTAINER  |   |               |                                      |               |         |   |  |
|--|--|---|---------------|--------------------------------------|---------------|---------|---|--|
| 102  |  |   |               | -                                    | which i       | is desc | ribed and                                     |  |
|  | claimed in: $\Box$ the attached specification $oxdot{M}$ the specification in application Serial No. <u>09/509,317</u> , filed <u>March 23, 2000</u>   |   |               |                                      |               |         |   |  |
|  | and (if applicable) amended on March 23  | (for declaration not accompanying application papers) |               |                                      |               |         |   |  |
|  | ☐ international (PCT) application No.  | filed   |               |                                      | and           |         |   |  |
|  | ☐ international (PCT) application No<br>as amended on  | (if any).   |               |                                      |               |         |   |  |
| applic<br>patent<br>for pa<br>below<br>in the<br>States<br>Regula        | I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.  I acknowledge the duty to disclose information of which I am aware which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations.§1.56(a).  I hereby claim the benefit of priority, under Title 35, United States Code, §119, of any foreign application(s) for patent or inventor's certificate listed in Item 103 below and have also identified in Item 103 below any foreign application(s) for patent or inventor's certificate having a filing date before that of the application for which priority is claimed.  I hereby claim the benefit, under Title 35, United States Code, §120, of any U.S. application(s) listed in Item 105 below. If this application is a continuation in part, insofar as the subject matter of any of the claims thereof is not disclosed in the prior U.S. application(s) identified in Item 105 below in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior U.S. application(s) identified in Item 105 below and the national or PCT international filing date of this application. |   |               |                                      |               |         |   |  |
| 1  | FOREIGN APPLICATION(S), IF ANY, FILED WITHIN 12 (6 if a Design) MONTHS PRIOR TO THE FILING DATE OF THIS APPLICATION  |   |               |                                      |               |         |   |  |
| 3  | COUNTRY  | APPLICATION NUMBER                                    |               | DATE OF FILING<br>(day, month, year) |               | T (     | PRIORITY<br>CLAIMED<br>UNDER<br>35 U.S.C. 119 |  |
|  | Germany  | 19742548.8  |               | 26 September 1997                    |               |         | YES X<br>NO                                   |  |
|  | PCT  | PCT/EP98/06056  |               | 24 September 1998                    |               |         | YES X<br>NO                                   |  |
|  | ALL FOREIGN APPLICATIONS, IF ANY, FILED MORE THAN 12 (6 if a Design) MONTHS PRIOR TO THE FILING DATE OF THIS APPLICATION   |   |               |                                      |               |         |   |  |
| 1 1  |  |   |               |                                      |               |         |   |  |
|  |  |   |               |                                      |               |         |   |  |
| <del></del>  |  | <del>_</del>  |               |                                      | <del></del> - |         |   |  |
| 1  | THIS APPLICATION IS A:   |   | SERIAL N      | 0.:                                  |               | FILED   | ):  |  |
| 0 CONTINUATION CONTINUATION-IN-PART 5 DIVISION OF PRIOR U.S. APPLICATION |  |   | □Ab           | Abandoned                            |               |         |   |  |
| POWE   | R OF ATTORNEY: As a named inventor, I h  | ereby appoint the                                     | e following a | ttorney(ş) to pro                    | osecute t     | this ap | plication and                                 |  |

transact all business in the Patent and Trademark Office connected therewith.

KENNETH WATOV, REG. NO. 26,042 ALLEN R. KIPNES, REG. NO. 28,433

D-55276

SEND CORRESPONDENCE TO: DIRECT TELEPHONE CALLS TO: WATOV & KIPNES, P.C. (name and telephone number) P.O. BOX 247 □ KENNETH WATOV PRINCETON JUNCTION, NJ 08550 M ALLEN R. KIPNES (609) 243-0330

Inventor(s) name must include at least one unabbreviated first or middle name. **FULL NAME** LAST NAME FIRST NAME MIDDLE NAME OF AIDAM ELKE INVENTOR 2 **RESIDENCE &** CITY OR OTHER-LOCATION STATE OR FOREIGN COUNTRY COUNTRY OF CITIZENSHIP WÖRTH **CITIZENSHIP GERMANY GERMANY** 0 POST OFFICE POST OFFICE ADDRESS CITY STATE OR COUNTRY ZIP CODE WÖRTH **ADDRESS** FORSTHAUS, **GERMANY** D-76744 LANGENBERG **FULL NAME** LAST NAME FIRST NAME MIDDLE NAME EBERT **MICHAEL INVENTOR RESIDENCE &** CITY OR OTHER LOCATION STATE OR FOREIGN COUNTRY COUNTRY OF CITIZENSHIP **CITIZENSHIP** WÖRRSTADT **GERMANY GERMANY** O POST OFFICE POST OFFICE ADDRESS CITY STATE OR COUNTRY ZIP CODE **ADDRESS** STAFFELWEG 4 WÖRRSTADT **GERMANY** D-55286 **FULL NAME** LAST NAME FIRST NAME MIDDLE NAME GROSSMANN OF TINO **INVENTOR** CITY OR OTHER LOCATION **RESIDENCE &** STATE OR FOREIGN COUNTRY COUNTRY OF CITIZENSHIP 2 **CITIZENSHIP** MAINZ **GERMANY GERMANY** POST OFFICE ADDRESS POST OFFICE CITY STATE OR COUNTRY ZIP CODE 3 FREIHERR-VORN-STEIN-**ADDRESS** MAINZ **GERMANY** D-55131 STRASSE 28 LAST NAME **FULL NAME** FIRST NAME MIDDLE NAME WERNER OF HEIL **INVENTOR RESIDENCE &** CITY OR OTHER LOCATION STATE OR FOREIGN COUNTRY COUNTRY OF CITIZENSHIP **VARCES ALLIERS ET RISSE**T FRANCE **CITIZENSHIP** FRANCE-GERMANY GER MANY OPPENHELM POST OFFICE POST OFFICE ADDRESS CITY STATE OR COUNTRY ZIP CODE LA GIRAUDIÈRO VARCES ALIERS ET **ADDRESS** FRANCE F-38760 AM GUTLEUT HAUS ·RISSET GERMANY OPPENHEIM 2

☑ Additional matter on page 3

| 500         |                             |  |   |                        |                                   |  |                     |
|-------------|-----------------------------|--|---|------------------------|-----------------------------------|--|---------------------|
|             | FULL NAME<br>OF<br>INVENTOR | LAST NAME<br>OTTEN   | FIRST NAME<br>ERNST-WILHELM                     |                        |                                   | MIDDLE NAME  |                     |
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| 5           | POST OFFICE<br>ADDRESS      | POST OFFICE ADDRESS<br>CARL-ORFF-STRASSE 47  |   |                        | STATE OR COUNT<br>GERMANY         | RY   | ZIP CODE<br>D-55127 |
|             | FULL NAME<br>OF<br>INVENTOR | LAST NAME ROHE   | FIRST I   |                        |                                   | MIDDLE NAME  |                     |
| 2<br>0<br>6 | RESIDENCE &<br>CITIZENSHIP  | CITY OR OTHER LOCATION  **OBLENZ**  **Bac***  **Fraction**  **Comparison**  ** | STATE OR FOREIGN COUNTRY GERMANY Switzerland    |                        | COUNTRY OF CITIZENSHIP<br>GERMANY |  |                     |
|             | POST OFFICE<br>ADDRESS      | POST OFFICE ADDRESS  | CITY STATE OR COUNT  KOBLENZ  Base Suritzer law |                        | •                                 | ZIP CODE<br><del>D-56070</del><br>こせー <b>く65</b> 6 |                     |
|             | FULL NAME<br>OF<br>INVENTOR | LAST NAME TO FI  |   | FIRST NAME<br>REINHARD |                                   | MIDDLE NAME  |                     |
| 2           | RESIDENCE &<br>CITIZENSHIP  | CITY OR OTHER LOCATION MAINZ   | _   | STATE OR FO<br>GERMANY | REIGN COUNTRY                     | COUNTRY OF CI<br>GERMANY                           | TIZENSHIP           |
| 7           | POST OFFICE<br>ADDRESS      | POST OFFICE ADDRESS<br>WILLI-WOLF-STRASSE 22   | CITY<br>MAINZ                                   | i                      | STATE OR COUNTI<br>GERMANY        | RY   | ZIP CODE<br>D-55128 |

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

| signature of inventor 201<br>E. A'dow | SIGNATURE OF INVENTOR 202 | SIGNATURE OF INVENTOR 203          |
|---------------------------------------|---------------------------|------------------------------------|
| DATE 21.4.00                          | DATE 14. 4. 00            | DATE 14.04,2000                    |
| SIGNATURE OF INVENTOR 204             | SIGNATURE OF INVENTOR 205 | SIGNATURE OF INVENTOR 206  D. Tale |
| DATE 14.4.00                          | DATE 14.4.00              | DATE 14.4.00                       |
| SIGNATURE OF INVENTOR 207             |                           |                                    |
| DATE 7 April 2000                     |                           |                                    |

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